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Study on the Fabrication and Characterization of Piezoelectric Paper made with Cellulose

•Prof. Jaehwan Kim

Center for EAPap Actuator
Department of Mechanical Engineering
Inha University
253 Yonghyun-Dong, Nam-Ku, Incheon 402-751, South Korea
email: jaehwan@inha.ac.kr, webpage: www.EAPap.com

ABSTRACT

This report deals piezoelectric paper made with cellulose by mechanically and electrically aligning regenerated cellulose films. Cellulose electro-active paper was prepared by dissolving cotton pulp in LiCl/*N, N*-dimethylacetamide solution and regenerating cellulose chains. An electric field was applied in the mechanical direction of cellulose films along with mechanical stretching. Alignment of cellulose chains was investigated in terms of applying electric field. The characteristics of cellulose films were analyzed by X-Ray diffractometer, Field emission scanning electron microscopy and High voltage electron microscopy. By applying the electric field, nanofibers of cellulose were generated and the crystallinity index was increased. When the piezoelectric charge constant was measured, it was gradually improved as increasing the applied electric field, which was associated with the increased cellulose crystallinity as well as the alignment of cellulose chains.

Keywords: Piezoelectric paper, Cellulose, Mechanical stretching, Electric field alignment, Fiber alignment, Electro-Active paper.

1. Introduction

Cellulose is one of the most naturally abundant biopolymers. Cellulose has been utilized in many fields due to its biocompatibility and chirality for the immobilization of proteins, antibodies as well as the formation of cellulose composites with synthetic polymers and biopolymers. Cellulose derivatives have been used for coatings, laminates, optical films and pharmaceuticals (Klemm et al. 2005) For cellulose derivatisation, homogeneous reaction condition is important and it can solve the problem related with polymer degradation and product heterogeneity (Ramos et al. 2005). N,N-dimethylacetamide (DMAc)/ Lithium Chloride (LiCl) solvent system has been widely used to make quickly, easily and reproducibly dissolved cellulose (Dupont 2003). Regenerated cellulose film has been fabricated by curing cellulose dissolved in the solvent system. By mechanically stretching the regenerated cellulose in wet state, chains in cellulose matrix

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14. ABSTRACT
This report deals piezoelectric paper made with cellulose by mechanically and electrically aligning regenerated cellulose films. Cellulose electro-active paper was prepared by dissolving cotton pulp in LiCl/N, N-dimethylacetamide solution and regenerating cellulose chains. An electric field was applied in the mechanical direction of cellulose films along with mechanical stretching. Alignment of cellulose chains was investigated in terms of applying electric field. The characteristics of cellulose films were analyzed by X-Ray diffractometer, Field emission scanning electron microscopy and High voltage electron microscopy. By applying the electric field, nanofibers of cellulose were generated and the crystallinity index was increased. When the piezoelectric charge constant was measured, it was gradually improved as increasing the applied electric field, which was associated with the increased cellulose crystallinity as well as the alignment of cellulose chains.

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has been aligned (Kondo et al. 2001; Kondo et al. 2004; Gindl et al. 2006). Moreover, many researchers have given their efforts to align cellulose with electric field or magnetic field (Kondo et al 2001; Sugiyama et al. 1992; Kimura et al. 2005; Bordel et al. 2006). However, people have not paid their attention on improving piezoelectric effect in aligned cellulose film, although small piezoelectric effect in cellulose has been reported long time ago (Fukada 1968).

Recently, cellulose has been discovered as a smart material that can be used as sensor and actuator materials (Kim et al. 2006[a]; Kim et al. 2006[b]). This smart material is termed as electro-active paper (EAPap) (Kim et al. 2002). EAPap has many advantages in terms of lightweight, dryness, low cost, biodegradability, large deformation, low actuation voltage and low power consumption. EAPap actuator is electrically activated due to a combination of ion migration and piezoelectric effects. Once piezoelectric effect is maximized in EAPap, then this material can be used for many applications such as sensors, microelectro-mechanical systems, speakers, microphones, transducers, and so on. The improvement of the piezoelectric effect in cellulose is strongly associated with the alignment of cellulose chains.

In this research, we investigated the alignment of cellulose chains in regenerated cellulose films by applying electric fields and mechanical stretching. Characteristics of the regenerated cellulose were analyzed by their X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and High voltage electron microscope (HVEM). The piezoelectricity of the aligned regenerated cellulose was evaluated by measuring their direct piezoelectric charge constant [d_{31}].

2. Experimental

2.1 Cellulose film preparation

The cotton pulp (MVE, DPw 4580) was purchased from Buckeye Technologies Co., USA. Its alpha cellulose is 99.3 %, dry basis weight is 569.5 g/m^2 and the dry density is 0.581 g/cm^3 that has the degree of polymerization, 4500 was torn in small pieces. The cotton pulp and LiCl (Junsei Chemical) was heated in oven at 100℃ to evaporate water. The cotton pulp was mixed with LiCl/anhydrous DMAc (*N,N*-dimethyl acetamide) (Aldrich) in proportion of cotton cellulose pulp/LiCl/DMAc to 2/8/90. The cellulose was dissolved in the solvent by heating at 155℃ with mechanical stirring according to the solvent exchange technique (El Seoud et al. 2000). The cellulose solution was spincoated on a silicon wafer. It was cured in solvent mixture, which is composed of deionized (DI) water and Isopropyl alcohol (IPA), for 3 hours to effectively eliminate Li^+ ions as well as DMAc (Yun et al. 2008). The cured film was rinsed twice in DI water.

2.2 Mechanical stretching

The wet cellulose film was clamped on the fixture of stretching equipment and stretched with 50% strain. To maintain the aligned cellulose chains, the stretched cellulose film was dried for 1 hour by exposing near infra-red ray, which was fixed above the film with 30cm distance.

2.3 Electrical field alignment

Cellulose chain alignment in regenerated cellulose was attempted by applying electric field along the mechanical stretching direction. The electric field alignment was

performed with the mechanical stretching. For the alignment, wet cellulose film was fixed on the stretching equipment and an electric field was applied on the cellulose film after uniaxial stretching with 50% strain. Figure 1 shows the mechanical stretching and electric field alignment process. Two electrodes were installed at the center of wet-stretched cellulose films with 5mm distance. The width of electrode is 10mm. DC electric field was applied to the electrode via voltage amplifier (Trek, PZD 350M/S). During the process, the regenerated cellulose was dried.

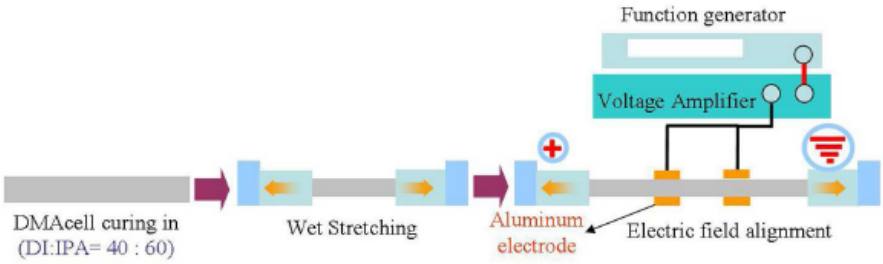

Figure 1 Electric field alignment process of regenerated cellulose with stretching.

2.4 Characterization

X-Ray diffraction patterns of regenerated cellulose samples were obtained by thin film X-Ray diffractometer (X'pert MPD, Philips). The X-Ray patterns were taken on flat films using nickel-filtered CuKα radiation supplied by X-ray generator at 40kV and 30mA. The patterns were recorded at 2θ from 5° to 40° under scanning rate of 0.015°/s. Cross-sectional morphologies of the samples were taken by FESEM (Hitachi, S-4000) and HVEM (JEOL, ARM 1300S). To prepare the cross-sectional HVEM sample, regenerated cellulose was molded in epoxy, and cured at 60℃ for 12 hours. Cryo ultra-microtome (Leica, EM Ultracutcult FCS) with diamond knife (PE-4006-B, elementsix™) was used to prepare epoxy-embedded thin membrane (< 70nm). The membrane was attached on a carbon coated TEM grid (IGC 200, PELCO®), and dried in vacuum oven at 40℃ for 12 hours. For staining, 2% Osmium tetraoxide was evaporated on the membrane. Finally, the cross-sectional image of HVEM sample was taken by a GATAN Model SP100W camera.

The surface image of the regenerated cellulose sample was seen by HVEM. To prepare the surface HVEM sample, cellulose solution was cast on a silicon wafer by spin-coating with 3000rpm and cured in DI (Deionized) water/Isopropyl alcohol (IPA) and rinsed in DI water. The prepared wet cellulose film was stretched and electrically poled as mentioned previously. TEM grid (without carbon membrane) (G200, EMS) was attached on the cellulose film before drying it. The thickness of the dried cellulose film was less than 100nm. This thickness was enough to meet the requirement for HVEM observation. For staining, 2% Osmium tetroxide was evaporated on the cellulose film.

2.5 Piezoelectric charge constant measurement

To characterize the piezoelectricity, the induced charge of the cellulose EAPap was measured by quasi-static method. Figure 2 shows the experimental setup for induced charge measurement that consists of a pull test machine, an environmental chamber and piccoammeter (Keithley, 6485). In the pull test machine, load cell (Daecell, UU-K010) and

linear scaler (Sony, GB-BA/SR128-015) were used to measure the applied load and displacement. Regenerated cellulose on which gold electrodes were coated on both sides was installed in the pull test machine by gripping the sample with the ASTM standard grip for polymer film tests. The electrodes were wired to piccoammeter and Labview was used to acquire the displacement, force and induced charge data. The induced charge during the pull test was measured by the piccoammeter. Strain rate was designated to 0.005mm/s and the test temperature and humidity conditions were 24℃ and 20-25%RH. Once the induced charge is measured, in-plane piezoelectric charge constant can be found as (ANSI/IEEE Std. 2000)

$$d_{31} = \frac{\text{Induced charge per unit electrode area}}{\text{Applied in - plane normal stress}} [\text{C/N}]$$

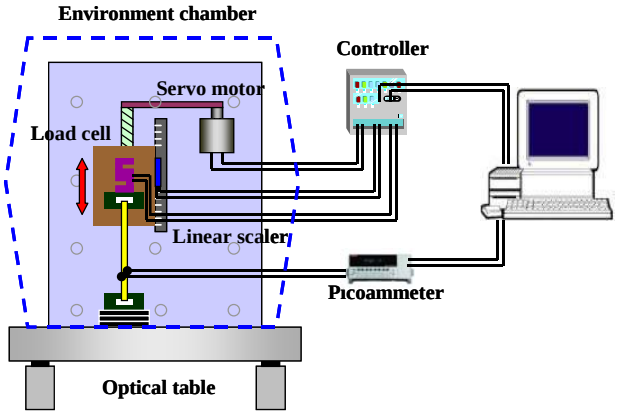

Figure 2 Induced charge measurement system.

3. Results and Discussions

3.1 Characterization

Regenerated cellulose has amphiphilic characteristics due to the presence of hydroxyl groups on anhydroglucose units. The cellulose molecules can be ordered in direction of stretching as well as electric field and the ordered cellulose consists of crystalline and noncrystalline. In wet state, water molecules interact with hydroxyl group of cellulose, and it causes increased mobility of cellulose chains due to weaken inter-intramolecular hydrogen bonds of cellulose (Olsson et al. 2004). The weaken hydrogen bonds can contribute to order cellulose chains in the direction of stretching or electric field. To investigate the electric field effect in the mechanically stretched cellulose films, different electric fields were applied to the regenerated cellulose films in wet state. The characteristics were investigated by XRD, SEM and HVEM. Figure 3 shows the XRD patterns. As increasing the applied electric field from 0V/mm to 40V/mm, 12.1° plane directional peak was clearly appeared and 22° directional peak was shifted to 23.5°. It might be due to strain relaxation or lattice deformation occurred by reorientation of cellulose. Originally, cellulose II has three reflection peaks of 12.1°, 19.8° and 22° for (110), $(1\bar{1}0)$ and (200), respectively. Regenerated cellulose has shown a diffused XRD profile comparing with cellulose II, which might be caused by slow coagulation of regenerated cellulose (Kondo et al. 2001). The XRD profile was not significantly changed

by the stretching process. The crystallinity index (CI) of the films was evaluated according to the reference (Wang et al. 2008). The first column of Table 1 shows the crystallinity index (IC) of the cellulose films according to the applied electric field. The CI was increased from 0.73 to 0.86 with the applied field increase from 0 to 40V/mm.

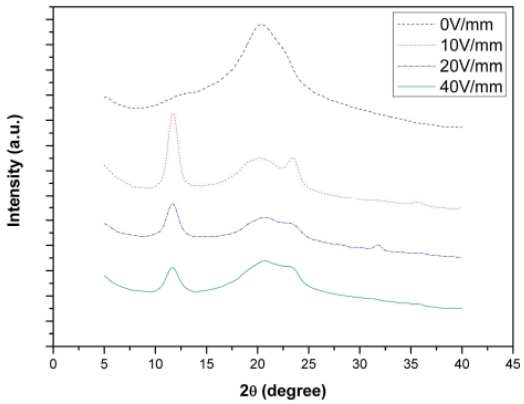

Figure 3 X-Ray diffraction pattern of regenerated cellulose after electric field alignment with stretching.

To investigate morphological changes with the applied electric field, the cross-sectional morphologies were taken by SEM and HVEM. Recently, the structure of regenerated cellulose was found to be a layered formation in thickness direction, and nematic ordered cellulose layers were oriented by wet stretching in uniaxial direction (Kondo et al. 2001). As shown in Fig. 4a, the regenerated cellulose also exhibited the layered structure. Notice that, after stretching the regenerated cellulose in wet state, a nanofiber formation in the cellulose matrix was observed (Fig. 4b). The nanofiber formation was changed according to the applied electric field. As comparing it with the stretched only cellulose film, the configuration of nanofibers was changed to a slender rod, getting uniform distribution in the cellulose matrix. As increasing the applied electric field up to 40V/mm, this trend of nanofiber formation was getting clear. This morphological change clearly depends on the increased crystallinity, which can influence the piezoelectricity of the cellulose films. For further understanding, the nanofiber structure was investigated using HVEM. Figure 5(a) shows the cross-section of the regenerated cellulose film under 40V/mm electric field and 50% stretching strain. Nanofibers in the range of 30 nm ~ 150 nm diameter can be seen in amorphous cellulose matrix. Figure 5(b) shows the surface HVEM image of the regenerated cellulose sample. Cellulose chains can be clearly seen in the surface image, and a zoomed in figure of the cellulose chains is seen in the upper right corner. The chain width and the distance between two parallel chains were measured using Digital Micrograph software (version 3.6.1). As the result, the average chain width was found to be 0.430nm ±0.036nm with the average chain distance of 0.474nm±0.042nm. This average chain width is similar to the average chain width of 0.462 nm for nematic ordered cellulose reported by Kondo et al. 2001. The increased crystallinity index might be associated with this nanofiber formation. As this nanofiber formation of cellulose increased by the stretching and electric field, the CI increased, and it improved the piezoelectric effect in cellulose films.

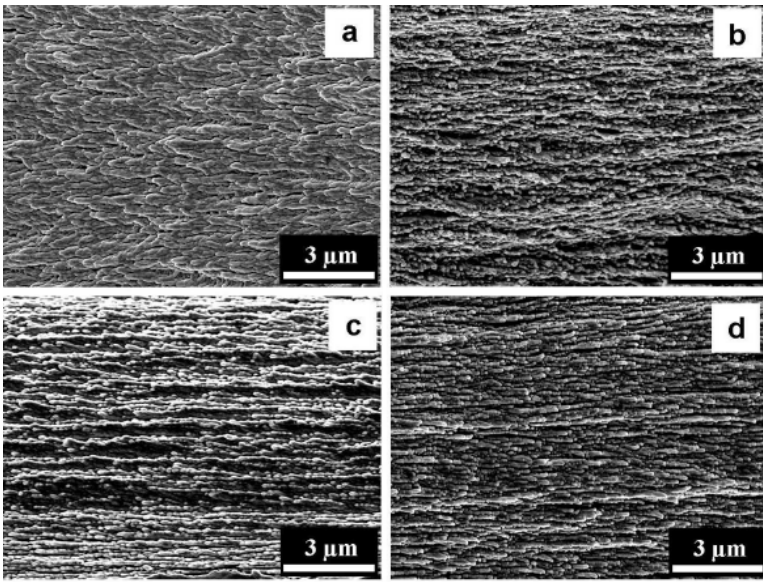

Figure 4 SEM cross-sectional images of regenerated cellulose with stretching ratio/ electric field: a) (1.0)/(0V/mm), b) (1.5)/(0V/mm), c) (1.5)/(20V/mm) and d) (1.5)/(40V/mm).

3.2 Piezoelectric charge constant measurement

Stretched regenerated cellulose films were prepared by applying different electric fields. Their piezoelectric charge constant was measured according to the method described before. The second column of Table 1 shows the measured in-plane piezoelectric charge constant [d_{31}]. Three samples for each electric field case were tested and the average value and its error were found. When the applied electric field was increased up to 40V/mm, the piezoelectric charge constant gradually increased, and it reached to 10.6 ±0.77 [pC/N] However, due to the thermal damage of samples occurred by high leakage current, the applied electric field was limited to 40V/mm in wet state. Although there was limitation of the applied electric field to cellulose films, this d_{31} value is higher than that of stretched and corona poled polyvinyl chloride films of 7.2 ±1.1 [pC/N] (Bharti et al. 1997). Once the regenerated cellulose films are well aligned by applying electric field with mechanical stretching over 50% strain, its piezoelectricity would be comparable with PVDF piezoelectric polymer. The piezoelectric cellulose films can be potentially used for many applications such as sensors, speakers, microphones and transducers, owing the merits of cellulose in terms of biodegradability, biocompatibility and low price.

Table 1. Crystallinity Index and piezo. constant of piezoelectric paper with electric field.

Electric field [V/mm]	Crystallinity Index [IC]	Piezoelectric charge constant [d_{31}]
0	0.73	2.3 ±0.13
10	0.81	3.1 ±0.18
20	0.83	5.4 ±0.36
40	0.86	10.6 ±0.77

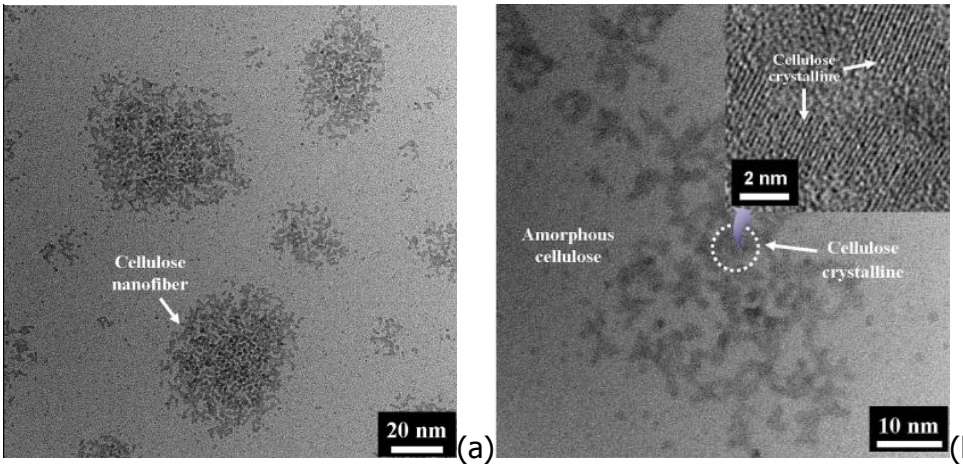

Figure 5 HVEM cross-sectional image of nanofibers in regenerated cellulose: (a) prepared by applying 40V/mm electric field and stretching with 50% strain, (b) Magnified HVEM surface image.

4. Conclusions

In this paper, electrically aligned cellulose films for Electro-Active Paper were made and the field effect was investigated. Characteristics of the regenerated cellulose films were investigated by taking XRD, SEM and HVEM. Piezoelectricity of the regenerated cellulose was evaluated by measuring the piezoelectric charge constant [d_{31}]. By applying electric field to the regenerated cellulose film under stretching, fine nanofibers were generated that were densely arranged in the cellulose matrix along the stretching direction. As increasing the electric field up to 40V/mm, the crystallinity index was increased by 18%. The generation of fine nanofibers with well alignment in stretching direction as well as increased crystallinity index improved the piezoelectricity of regenerated cellulose films. This improved piezoelectric effect is important for potential applications of sensors, speakers, microphones, transducers, and so on.

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